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Photocatalytic Properties of Ag@AgCl-RGO Composites

Xiuye Yan[a*], Shunjin Peng[b], Haihua Zhu[a]

[a]*College of Material and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, Hubei Province, P.R. China*
[b]*College of Science, Wuhan University,Science and Technology, Wuhan 430081, Hubei Province, P.R. China*

Abstract

Ag@AgCl-RGO composite photocatalyst with both graphene's special electronic state structure and Ag@AgCl's excellent visible light catalytic performance was fabricated. Phase composition of the photocatylst were characterized using X-ray diffraction. Scanning electron microscope and UV-vis absorption spectra characterize the surface morphology and spectroscopic properties. The RhB dye concentration was measured by UV-Vis spectra with the changes , the catalytic performance of different photocatalyst was tested, the mechanism of Ag@AgCl-RGO catalyzed degradation of RhB was explored in the presence of the catalyst. The research results show that the visible light absorption capacity and catalytic efficiency of Ag@AgCl-RGO was better than Ag@AgCl.

Key words: photocatalyst, Ag@AgCl, graphene oxide, reduced graphene oxide, Rhodamine B

Energy crisis and environmental pollution caused by economic development have become one of the most important challenges nowadays. The related research and development about the photocatalytic technology such as photocatalytic water splitting, photocatalytic degradation of organic pollution, photocatalytic decomposition of carbon dioxide has been concerned by the scientists around the globe[1-3]. Over the years, researchers have been being committed to the development of new types of photocatalytic materials and modifying the traditional photocatalytic materials to improve its visible visible light catalytic efficiency , which has made great progress[4,5]. Recently, it is found that nobel metal nanocrystal (such as Pt and Ag) with

* Corresponding Author:Tel. 13429830315
E-mail address :yanxiuye@163.com,

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a surface plasmon resonance exhibits photocatalytic activity under visible light irradiation**,** which provide new ideas and direction for the research and development of the visible light photocatalytic materials[6, 7]. plasmonic photocatalysts such as Ag@AgCl have been be synthesized with a good catalytic performance[8, 9]. Nevertheless Ag@AgX particles with micrometers size may cause plasmon-induced electron-hole pairs recombined in a high rate in the process of transfering to the photocatalyst surface[10]. Graphene oxide (GO) as the precursor for graphene has good solution-dispersibility and can be prepared easyly . Reduced-GO (RGO) hybrids with metal oxide would improve its photocatalytic activity through modulate its electronic structure and extract the excited charge carriers [10,11].

Herein, composite photocatalyst, Ag@AgCl-RGO was designed, which has both graphene's special electronic state structure and Ag@AgCl excellent visible light catalytic performance using photoreducing AgCl/GO composites prepared by ion-exchange method. Phase composition of the photocatylst was characterized using X-ray diffraction. Scanning electron microscope and UV-vis absorption spectra characterize the surface morphology and spectroscopic properties of the samples. The catalytic performance of different sample was characterized by measuring the Rhodamine B (RhB) degradation rate in solution. Finally experimental results show that our Ag@AgCl-RGO samples have a better visible light absorption capacity and catalytic efficiency than Ag@AgCl.

1. Experimental section

1.1 Material

Silver nitrate (AgNO3) supplied from Wuhan Air Force four station; Sodium molybdate (Na2MoO4) supplied from Sinopharm Chemical Reagent Co., Ltd; Concentrated hydrochloric acid (HCl, the mass fraction of 36%-38%) supplied from Zhongping Kaifeng Dongda Chemical Reagent Co., Ltd; Natural flake graphite supplied from Qingdao Xinyuan Graphite milk company (Limited carbon content > 97%). All other chemicals used are of analytical grade, and the the deionized water was obtained by a secondary distillation.

1.2 Synthesis of Ag@AgCl-RGO Composite

1.2.1 Synthesis of Ag_2MoO_4-GO Composite

We prepared GO firstly by a modified Hummers et al. Method[12]. Ag_2MoO_4-RGO were synthesised as following: GO (20.7 mg) was dispersed to Na_2MoO_4 aqueous solution(40 ml, 0.1 mol L^{-1}) after stirred for 12 h. Next, $AgNO_3$ aqueous solution(40 ml, 0.2 mol L^{-1}) was added slowly and then diluted NaOH solution was added followed to the mixture until its pH value was adjusted to 8.0. After 0.5 h stirred of stirring, we transferred the resulting solution into a special teflon autoclave, in which the solution was heated at 180 ºC for 2 h. After natural cooled, we collected the precipitate Ag_2MoO_4-RGO composite and washed it until its pH value reached about 7.

1.2.2 Synthesis of AgCl-GO composite

AgCl-GO composites was synthesized by a ion-exchange rection. Ag_2MoO_4-GO composites was soaked in an excess of concentrated hydrochloric acid and then sonicated for 0.5 h until the ion-exchange step was completed . AgCl-GO composite could be obtained after collecting and washing the precipitate until the pH value reached about 7.

1.2.3 Synthesis of Ag@AgCl-RGO composite

We synthesize the Ag@AgCl-RGO composite through a photoreduced procedure. A mount of AgCl-GO composties was put into a water solution with a little methanol ,which was then irradiated under UV light for 10 min, through which was dried in air, Ag@AgCl-RGO was synthesized completely.

Different Ag@AgCl-RGO photocatalysts was prepared depending on the amount of GO following this procedure. Pure Ag@AgCl without GO was also synthesised for contrast experiment.

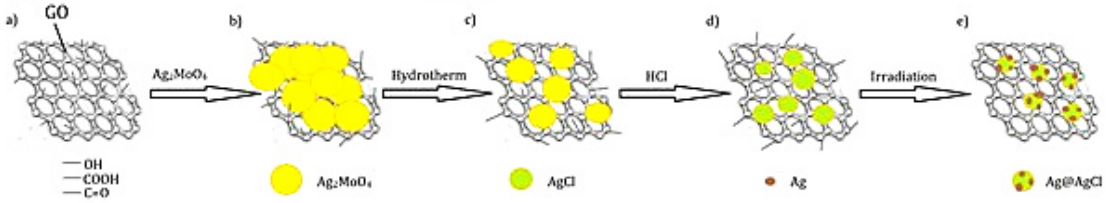

Fig.1 Schematic of fabricate of Ag@AgCl-RGO composite

1.3 Organizational Structure, Morphology and Optical Properties Characterization

X-ray diffractometer (XRD) patterns (PHILIPS XPert pro MPD) were recorded in the 2□ region of 10º-90º, using Cu Ka radiation (λ=154056,U=40 KV,I=40 mA). Scanning electron microscopy (SEM, PHILIPS XL30 TMP) was used to examine the microstructures and surface morphologies of Ag@AgCl-RGO samples . The composites' optical absorbance spectra were obtained by a UV-vis spectrophotometer (Xipu TU－1901).

1.4 Evaluation on Photocatalytic property of Ag@AgCl-RGO Composite

We evaluated the photocatalytic property of Ag@AgCl-RGO composites by measuring the degradation rate of RhB. Firstly, we suspended a certain mount of photocatalyst (0.02 g) into 30 ml RhB solution (10 mg L^{-1}) and then stirred the mixture for 0.5 h in dark. A CHFXM500 Xe arc lamp was used as the light source which equipped with a UV cutoff filter (λ>400 nm). The illumination intensity of the light was adjusted to 100 mW cm^{-2}**.** Every ten minutes under visible light irradiation, we collected 5 ml of reaction solution and centrifuged it to get the supernatant liquid, and then measure the RhB dye concentration using a UV-vis spectroscopy.

2. Results and Discussion

2.1 Synthesis of Ag@AgCl-RGO composite

The Ag@AgCl-RGO composite fabrication strategy consists of three-step procedure(scheme 1). Two synthesis methods of Ag@AgCl-RGO listed as following: (1) GO firstly dispersed to $AgNO_3$ solution after dropping Na_2MoO_4 solution; (2) GO firstly dispersed to Na_2MoO_4 solution and then dropping $AgNO_3$ solution. It is discovered that photocatalytic property of the samples synthesized by the second method is better than the first. On the surface of GO, we know there are several kind of functional groups. In GO suspension for the first method, Ag^+ was stabilized by these functional groups such as hydroxyl and then grown to Ag_2MoO_4 particles process subsequently, Ag^+ ion were wrapped between MoO_4^{2-} and GO surface because the radius of Ag^+ with respect MoO_4^{2-} very small. This wrapped structure on the one hand hindered the contact of Ag^+ and Cl^- to form AgCl in the ion-exchange process subsequently, on the other hand Ag^+ can not be reduced effectively to Ag^0 unless received light fully in the process of photoreduction. But in the method 2, Na^+ adsorption on the surface of GO firstly lead to MoO_4^{2-} enriched in GO outer surface and no special orientation of Ag_2MoO_4 deposition on the GO surface after adding Ag^+. Thus, Ag^+ and Cl^- can contact fully at the same time AgCl generation subsequently accept light easily.

2.2 Structure, Morphology and Optical Properties Properties of Ag@AgCl-RGO composite

The XRD patterns of Ag, AgCl and Ag@AgCl-RGO composites were shown in figure 2. In the figure, the characteristic peaks of each sample is acute, it shows that the samples have a high crystallinity degree, and there is no significant change in the peak value for different samples indicates that the crystallinity degree for Ag@AgCl-RGO basically unchanged with the increase of GO content. In addition, the XRD patterns for samples d and e were not appear characteristic peaks of the GO illustrate that GO has been sufficiently reduced to RGO[13].

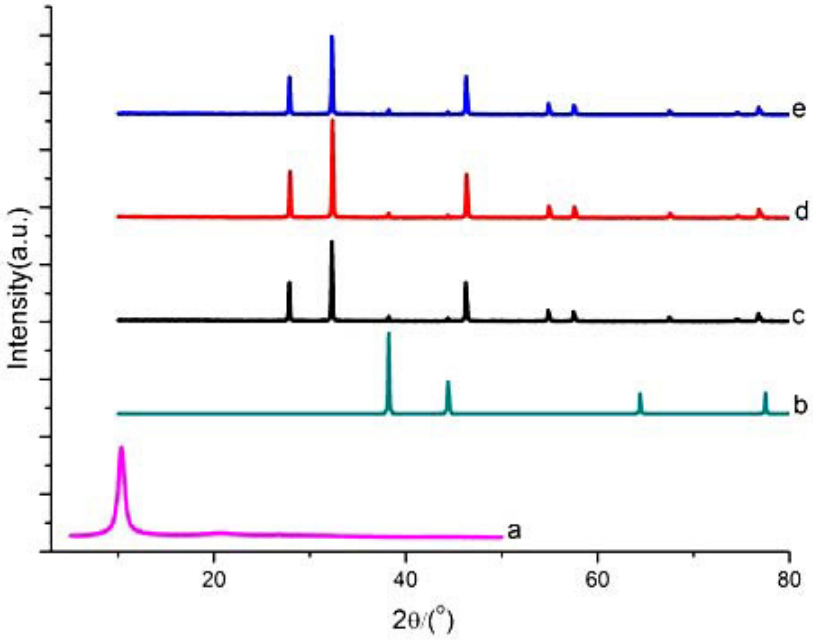

Fig. 2 XRD patterns of the samples (a) GO; (b) Ag particles; (c)Ag@AgCl; (d)Ag@AgCl-RGO(1.8 wt.%); (e)Ag@AgCl-RGO(3.6 wt.%)

Figure 3c and 3d show the typical surface morphology of the prepared Ag@AgCl-RGO samples. Compared with the pure Ag@AgCl particles (Figure 3a,3b), the particles on Ag@AgCl-RGO composite surfaces may be Ag particles with more uniformly distributed and smaller size(20-100 nm). Figure 3c and 3d also clearly showed that small pieces of the RGO layers inlaid between Ag branches and AgCl matrix, Ag@AgCl particles growth on RGO pieces' surface as a substrate.

Figure 4 shows their absorption spectra properties for these sythesized samples. For those samples, all of them exhibite strong absorption of visible light due to the Ag nanocrystal on their surface which have a strong surface plasmon resonance (SPR). For A@AgCl-RGO samples, the absorption edge move up and the visible light absorption capacity is also enhanced. So we can guess that GO sheets have been grafted on to the surface of Ag@AgCl nanoparticles partly. The other reason to enhance the absorption is that many branches structures formed on the surface of Ag@AgCl-RGO composites found from SEM images generate a secondary reflection. Nevertheless, the absorption is suppressed until the content of RGO further increase to

5.30 wt %, because the excess RGO wrapped the AgCl to reduce the illumination area of Ag^0.

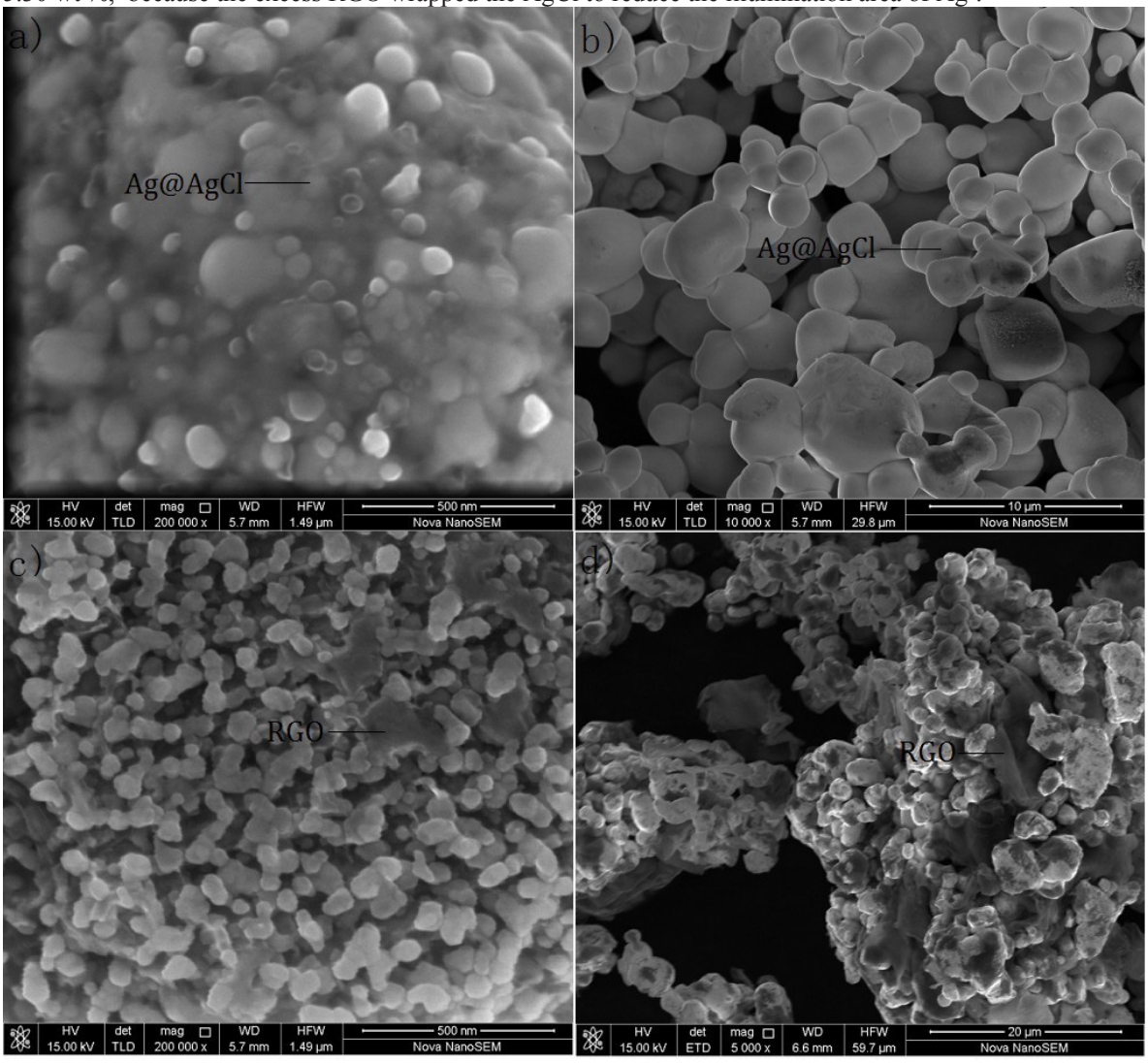

Fig.3 SEM images of the samples(a) and (b) Ag@AgCl; (C) Ag@AgCl-RGO(1.8 wt.%); (d)Ag@AgCl-RGO(3.6 wt.%)

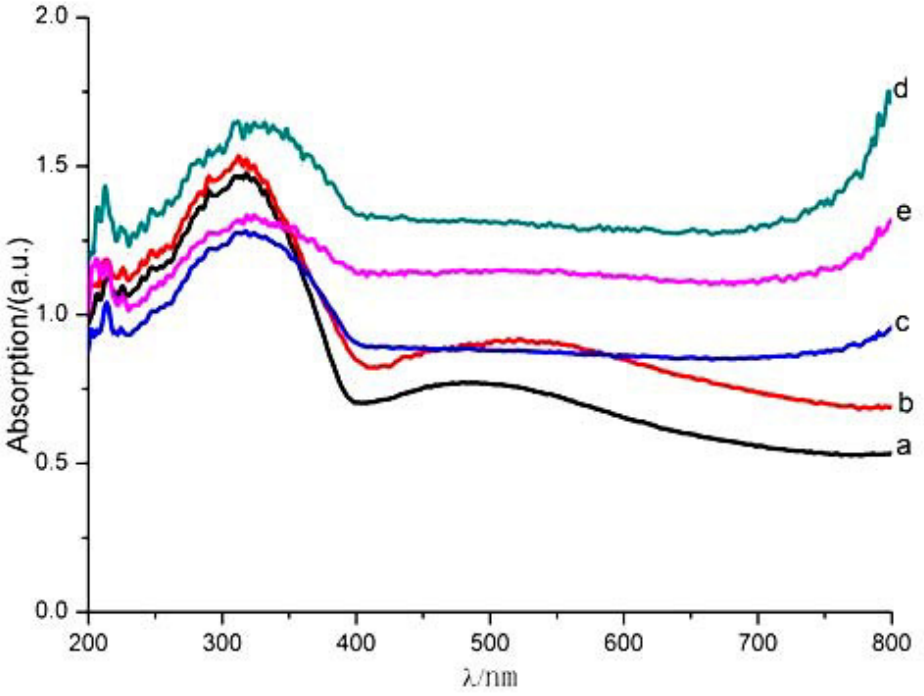

Fig.4 UV/Vis diffuse-reflectance spectra of the samples (a) AgCl; (b) Ag@AgCl-RGO(1.0 wt.%); (c) Ag@AgCl-RGO(1.8 wt.%); (d)Ag@AgCl-RGO(3.6 wt.%); (e) Ag@AgCl-RGO(5.3 wt.%)

2.3 Evaluation of Photocatalytic property

Figure 5 shows the concentration changes of RhB dye every 10 min . Clearly, RhB concentration in four samples decreased gradually duo to Ag nanocrystal on the surface whose SPR are sensitive to visible light. The samples' photocatalytic property of Ag@AgCl-RGO(1.8 wt.%) and Ag@AgCl-RGO(3.6 wt.%) were significantly better than Ag@AgCl, Because RGO pieces can reduce the resistance of separating and transporting charge generated from Ag nanocrystal. But when RGO content increased to 5.3%, the photocatalytic performance of Ag@AgCl-RGO(5.3 wt.%) was close to Ag@AgCl because the excess RGO wrapped the Ag@AgCl particles to reduce the illumination area.

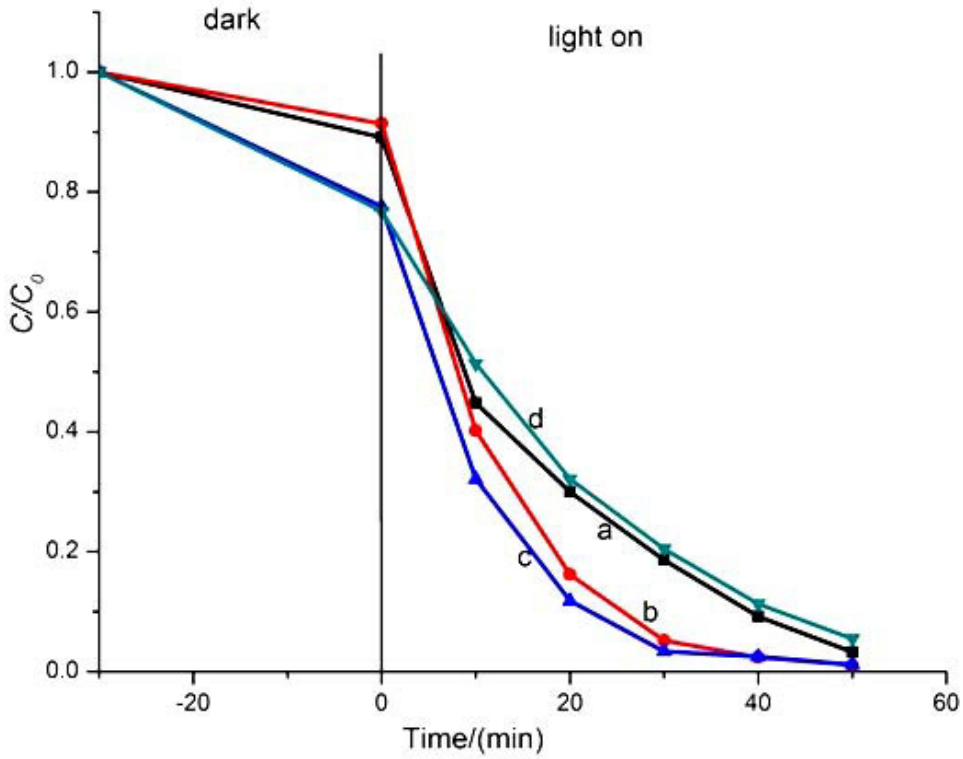

Fig.5 Photocatalytic property of the samples (a) AgCl; (b) Ag@AgCl-RGO (1.8 wt.%); (c) Ag@AgCl-RGO (3.6 wt.%); (d) Ag@AgCl-RGO (5.3 wt.%)

2.4 Photocatalytic Mechanism

It has been reported that AgCl particles is usually negatively charged because their surface is terminated by Cl^- ion. Free electrons which exist in the metallic Ag nanoparticles clear to the AgCl crystal surface are usually polarized. So electrons induced by SPR transfer to the the Ag nanocrystal's surface and then quickly transfer to RGO sheets , while holes shift to the interface of Ag nanocrystal and AgCl crystal under polarization field. So a better catalytic effect can be obtained through this process which increase the rate of charge separation.

Another reason of the catalytic efficiency is that Ag nanocrystal's visible light absorption capacity has also been enhanced duo to its electronic structure may be modulated when hybrid with RGO sheet.

A final reason is that RhB molecules would concentrate near the catalyst surface from solution in the presence of RGO sheets. Ag@AgCl and the dye moleculeswould be full contacted to promotes the photocatalytic property[14].

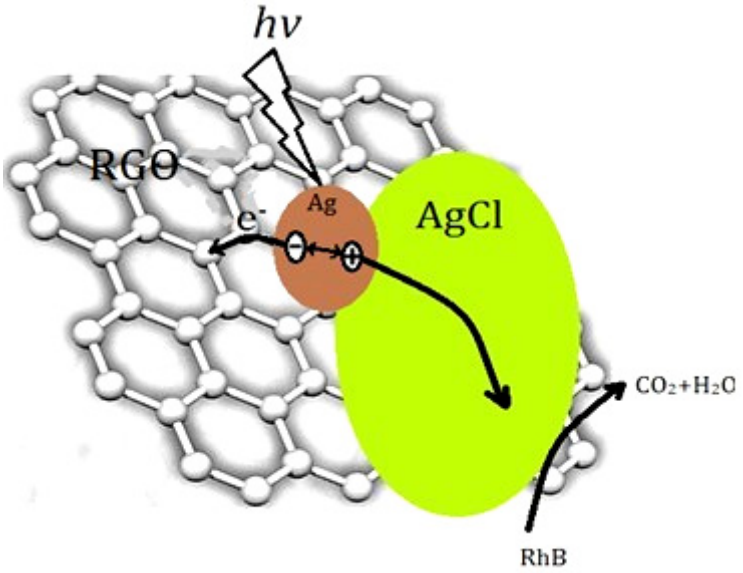

Fig.6 Schematic of mechanism for the enhanced of photocatalytic property of Ag@AgCl composite by the RGO in degradation of Rhodamine B

3. Summary

Ag@AgCl-RGO composite photocatalysts with better catalytic performance under visible light than Ag@AgCl have been successfully synthesized. The dispersion craft and content of RGO in catalyst Ag@AgCl-RGO composites have important effect on their catalytic performance. Ag@AgCl-RGO composite photocatalysts exhibits excellent photocatalytic property duo to increasing the rate of charge separation and enhancing the absorption of visible light of Ag nanocrystal. This catalyst has potentially application in environmental pollution.

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Contact of Corresponding Author: Xiuye Yan, yanxiuye@163.com, 13429830315